Activation of Terminal Alkynes at the Sulfur-Rich Bimetallic Site $[Mo^{III}_2Cp_2(\mu-SMe)_3]^+$: Alkyne–Vinylidene **Conversion and C-S and C-C Couplings Promoted by** Addition of Unsaturated Substrates (RC=CH, RN=C, S=C=S). Crystal Structures of μ - η^{1} : η^{2} -Vinylidene, μ - η^{1} : η^{2} -Acetylide, and μ - η^{1} : η^{3} -Vinyl-Thioether **Compounds**

Philippe Schollhammer, Nolwenn Cabon, Jean-François Capon, François Y. Pétillon,* and Jean Talarmin

UMR CNRS 6521, Chimie, Electrochimie Moléculaires et Chimie Analytique, Faculté des Sciences, Université de Bretagne Occidentale, BP 809, 29285 Brest-Cédex, France

Kenneth W. Muir*

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Great Britain

Received November 14, 2000

Reactions of the bis(nitrile) compound $[Mo_2Cp_2(MeCN)_2(\mu-SMe)_3](BF_4)$ (1) with terminal alkynes in a 1:1 ratio in dichloromethane at room temperature led to the alkyne adduct $[Mo_2Cp_2(\mu-SMe)_3(RCCH)](BF_4)$ (2: R = Tol (2a), Ph (2b), CH₃C=CH₂ (2c), nPr (2d), CO₂Me (2e), CF_3 (2f). Compounds 2a-d were readily deprotonated with Et_3N to give neutral acetylide derivatives $[Mo_2Cp_2(\mu-\eta^1:\eta^2-C\equiv CR)(\mu-SMe)_3]$ (3). Protonation of 3 afforded exclusively the vinylidene complexes $[Mo_2Cp_2(u-\eta^1:\eta^2-C=CHR)(u-SMe)_3](BF_3)$ (4). Reaction of 1 with an excess of terminal alkyne RCCH in dichloromethane gave either the six-membered metallacycle compounds $[Mo_2Cp_2(\mu-\eta^2:\eta^4-CR=CHCR=CHSMe)(\mu-SMe)_2](BF_4)$ (5) or the S-methylthiophenium derivatives $[Mo_2Cp_2(\mu-\eta^2:\eta^4-C_4H_2R_2SMe)(\mu-SMe)_2](BF_4)$ (6), depending on the nature of the R groups. Further reactions of the alkyne adducts 2 with isocyanide and carbon disulfide led to the vinyl-thioether complexes $[Mo_2Cp_2(\mu-\eta^1:\eta^3-CR=CR'-SMe) (\mu$ -SMe)₂(RNC)](BF₄) (7, 8) and to their CS₂ adducts [Mo₂Cp₂(S₂C–CR'=CRSMe)(μ -SMe)₂]- (BF_4) (9, 10), which arise from regioselective C-S coupling. A mechanism is proposed for the formation of the cyclic thiometalla compounds 5, 9, and 10 and of the thiophenium species **6** which assigns a key intermediate role to vinyl-thioether species. The molecular structures of **3a**, **4b**, and **7a** have been established by X-ray diffraction studies.

Introduction

This study of the interaction of alkynes with the sulfur-rich dimolybdenum system Cp₂Mo₂(µ-SMe)₃ was aimed at eliciting cooperative activation by the adjacent metals, leading to chemical transformations unattainable with a single metal atom.¹ Such studies also afford simple structural and chemical precedents for the behavior of less accessible natural or industrial catalyst systems.² Bimetallic complexes offer an attractive compromise between polymetallic activity and structural simplicity.³ The incorporation of bridging groups inhibits

fragmentation but may also affect the activity of the metal site.⁴ Though sulfur-containing bridges can stabilize robust polymetallic complexes, their activity has been relatively little explored because of the notoriety of sulfur derivatives as catalyst poisons.^{4b,c} In this respect, the sulfur-rich environment of the cofactors of some metalloenzymes⁵ and the well-developed chemistry of thiolato-bridged diruthenium and dimolybdenum systems are noteworthy.1c,d,4b,c

Recently, Rakowski DuBois and co-workers reported that the thermal lability of the thioether bridge in $[Mo_2Cp_2(\mu-S_2CH_2)(\mu-SMe)(\mu-SMe_2)]^+$ gave rise to sub-

^{(1) (}a) Catalysis by Di- and Polynuclear Metal Cluster Complexes, Adams, R. D., Cotton, F. A., Eds.; Wiley-VCH: New York, 1998. (b) Braunstein, P.; Rose, J. In *Chemical Bonds-Better Ways to Make Them* Braunstein, P.; Rose, J. In *Chemical Bonds-Better Ways to Make Them* and Break Them, Bernal, I., Ed.; Elsevier: Amsterdam, 1989; p. 5. (c)
Hidai, M.; Mizobe, Y. In *Transition Metal Sulfur Chemistry–Biological* and Industrial Significance, Stiefel, E. I., Matsumoto, K., Eds.; ACS
Symposium Series 653; American Chemical Society: Washington, DC, 1996; p. 310. (d) Hidai, M.; Mizobe, Y.; Matsuzaka, H. *J. Organomet. Chem.* 1994, 473, 1 and references therein.
(2) Henderson, R. A. J. Chem. Soc., Dalton Trans. 1995, 503.

⁽³⁾ For example: (a) Curtis, M. D. Polyhedron 1987, 6, 759. (b) Winter, M. J. Adv. Organomet. Chem. 1991, 29, 101.

⁽⁴⁾ For example: (a) King, J. D.; Mays, M. J.; Mo, C.-Y.; Raithby, P. R.; Rennie, M. A.; Solan, G. A.; Adatia, T.; Conole, G. J. Organomet. *Chem.* **2000**, *601*, 271 and references therein. (b) Rakowski DuBois, M. Polyhedron **1997**, *16*, 3089. (c) Rakowski DuBois, M. J. Cluster Sci. 1996, 7, 293.

^{(5) (}a) Richards, R. L. New J. Chem. **1997**, 21, 727. (b) Sellmann, D.; Sutter, J. Acc. Chem. Res. **1997**, 30, 460. (c) Coucouvanis, D. J. Bio. Inorg. Chem. 1996, 1, 594.

stitution and desulfurization reactions. They speculated that the active intermediate, which could be neither isolated nor characterized, was the unsaturated species $[Mo_2Cp_2(\mu-S_2CH_2)(\mu-SMe)]^+$, stabilized by coordinated solvent molecules.^{6,7} We have reported stoichiometric reactions which occur at a similar tris(*µ*-thiolato) bimetallic site in the μ -chloro complex [Mo₂Cp₂(μ -Cl)(μ -SMe)₃].⁸ This complex in MeCN solution afforded the stable and tractable bis(acetonitrile) species⁹ [Mo₂Cp₂- $(MeCN)_2(\mu$ -SMe)₃](BF₄) (1), which is similar to the unsaturated intermediate postulated by Rakowski DuBois. Recently, we have shown that **1** can add two terminal alkynes to its coordination sphere: formally regioselective head-to-tail and tail-to-tail linkage of the alkynes and their coupling to the sulfur atom of a thiolate bridge gave six-membered metallacycles or thiophenium derivatives.¹⁰ These results suggest that 1 may undergo formal insertion of alkynes into a Mo-S bond. The rarity of such processes, which are known only for certain mono- and bimetallic complexes containing fluorinated alkynes¹¹ and for diruthenium compounds,¹² and the opportunity to develop new routes to S-heterocycles¹³ have led us to investigate the reactivity of 1 toward terminal alkynes RC=CH.

We shall show that **1** reacts with various alkynes to afford the dinuclear alkyne adducts $[Mo_2Cp_2(\mu-SMe)_3-(RCCH)]^+$ (**2**), which are intermediates in the formation of thiametallacycles at the $\{Mo_2Cp_2(\mu-SMe)_3\}^+$ site, and in which the alkyne group may also undergo an 1,2-H shift, giving rise to vinylidene species. Furthermore, addition of unsaturated molecules (e.g., isocyanides) to **2** results in the formation of vinyl-thioether derivatives with an unprecedented μ - η^1 : η^3 -coordination. A preliminary communication of a part of this work has already appeared.¹⁰

(10) Capon, J. F.; Schollhammer, P.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W. Organometallics **1999**, *18*, 2055.

Metallics 1999, 14, 705. (d) Adams, H.; Anott, M.; Banctott, M. N.;
Morris, M. J. J. Chem. Soc., Dalton Trans. 2000, 4145.
(13) (a) Spencer, J.; Pfeffer, M.; De Cian, A.; Fischer, J. J. Org. Chem.
1995, 60, 1005. (b) Rauchfuss, T. B. Prog. Inorg. Chem. 1991, 39, 259.
(c) Linford, L.; Raubenheimer, H. G. Adv. Organomet. Chem. 1991, 32, 1. (c) Kondo, T.; Mitsudo, T. A. Chem. Rev. 2000, 100, 3205.

Results and Discussion

1. Reaction of [Mo_2Cp_2(MeCN)_2(\mu-SMe)_3](BF_4) (1) with an Equimolar Amount of Terminal Alkyne **RC=CH.** A red solution of **1** in dichloromethane reacted quantitatively with 1 equiv of RCCH (R = Tol, Ph, C(CH₃)=CH₂, *n*Pr, CO₂Me) and with 2–3 equiv of CF₃CCH at room temperature within 30 min to give brown or green solutions. Addition of diethyl ether precipitated complexes **2a**-**f** (eq 1) as brown or green



with either the more sterically hindered $tBuC \equiv CH$ or with disubstituted alkynes $RC \equiv CR$. The complexes 2 were unambiguously formulated by spectroscopic studies as the Mo^{III}-Mo^{III} alkyne adducts [Mo₂Cp₂(RCCH)- $(\mu$ -SMe)₃](BF₄), but the mode of coordination of the alkyne has not been reliably established, since monocrystals of diffraction quality could not be obtained. At room temperature the ¹H NMR spectra of **2** displayed both the resonances expected for the alkyne substituent, R, and a low-field signal (between 12 and 14 ppm) for the CH end of the alkyne, indicating coordination of an RCCH ligand to the molybdenum atoms. The single broad resonance which was observed for the two cyclopentadienyl groups suggested that a dynamic process was operative in solution at room temperature for complexes **2a**-**d**. Two cyclopentadienyl resonances were observed at room temperature for complexes 2e,f, which contain alkynes with the more electron-withdrawing groups COOMe and CF₃. ¹³C NMR spectra were recorded to get more information about the mode of coordination of the alkyne in 2. The two resonances of the sp-hybridized carbon atoms of the alkyne RCCH display some of the largest downfield chemical shifts yet reported for M₂(alkyne) complexes (between 254 and 291 ppm),¹⁴ lying in the carbene range but slightly lower than expected for four-electron-donor alkynes in mononuclear compounds.¹⁵ Such data do not allow the nature of the alkyne-metal bonding to be defined without ambiguity, especially as the strong deshielding observed in 2 may partially reflect the electronic behavior of the thiolato-bridged bimetallic cation. Nevertheless, they suggest that the alkyne acts as a four-electron donor with a significant π_{\perp} contribution,¹⁵ as required by the electron-counting rules to saturate the $\{Mo_2Cp_2(\mu SMe_{3}^{+}$ core. The alkyne coordination in **2** may not be completely described by either the classical tetrahedrane μ - η^2 : η^2 coordination mode (I; Chart 1)¹⁶ or the dimetallacyclobutene μ - η^1 : η^1 coordination mode (II;

⁽⁶⁾ Gabay, J.; Dietz, S.; Bernatis, P.; Rakowski DuBois, M. Organometallics 1993, 12, 3630.
(7) Tucker, D. S.; Dietz, S.; Parker, K. G.; Carperos, V.; Gabay, J.;

⁽⁷⁾ Tucker, D. S.; Dietz, S.; Parker, K. G.; Carperos, V.; Gabay, J.; Noll, B.; Rakowski DuBois, M.; Campana, C. F. *Organometallics* **1995**, *14*, 3630.

^{(8) (}a) Schollhammer, P.; Pétillon, F. Y.; Poder-Guillou, S.; Saillard, J. Y.; Talarmin, J.; Muir, K. W. *Chem. Commun.* **1996**, 2633. (b) Schollhammer, P.; Guénin, E.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W.; Yufit, D. S. *Organometallics* **1998**, *17*, 1922.

⁽⁹⁾ Barrière, F.; Le Mest, Y.; Pétillon, F. Y.; Poder-Guillou, S.; Schollhammer, P.; Talarmin, J. J. Chem. Soc., Dalton Trans. **1996**, 3967.

^{(11) (}a) Davidson, J. L.; Sharp, D. W. A. J. Chem. Soc., Dalton Trans.
1975, 2283. (b) Carlton, L.; Davidson, J. L.; Miller, J. C.; Muir, K. W. J. Chem. Soc., Chem. Commun. 1984, 11. (c) Carlton, L.; Davidson, J. L.; Ewing, P.; Manojlovic-Muir, L.; Muir, K. W. J. Chem. Soc., Chem. Commun. 1985, 1474. (d) Azelee Wan Abu Bakar, W.; Carlton, L.; Davidson, J. L.; Manojlovic-Muir, L.; Muir, K. W. J. Chem. Soc., Chem. Commun. 1985, 352, C54. (e) Agh-Atabay, N. M.; Canoira, L. J.; Carlton, L.; Davidson, J. L. J. Chem. Soc., Dalton Trans. 1991, 1175. (f) Carlton, L.; Agh-Atabay, N. M.; Davidson, J. L. J. Organomet. Chem. 1975. (g) Pétillon, F. Y.; Le Floch-Pérennou, F.; Guerchais, J. E.; Sharp, D. W. A. J. Organomet. Chem. 1979, 173, 89. (h) Guerchais, J. E.; Le Floch-Pérennou, F.; Pétillon, F. Y.; Keith, A. N.; Manojlovic-Muir, L.; Muir, K. W.; Sharp, D. W. A. J. Chem. Soc., Chem. Commun. 1979, 410.

^{(12) (}a) Nishio, M.; Matsuzaka, H.; Mizobe, Y.; Hidai, M. J. Chem. Soc., Chem. Commun. **1993**, 375. (b) Nishio, M.; Matsuzaka, H.; Mizobe, Y.; Tanase, T.; Hidai, M. Organometallics **1994**, 13, 4214. (c) Koelle, U.; Rietmann, C.; Tjoe, J.; Wagner, T.; Englert, U. Organometallics **1995**, 14, 703. (d) Adams, H.; Allott, M.; Bancroft, M. N.; Morris, M. J. J. Chem. Soc., Dalton Trans. **2000**, 4145.

^{(14) (}a) Bott, S. G.; Clark, D. L.; Green, M. L. H.; Mountford, P. J. Chem. Soc., Dalton Trans. **1991**, 471. (b) Feng, Q.; Green, M. L. H.; Mountford, P. J. Chem. Soc., Dalton Trans. **1992**, 2171.

⁽¹⁵⁾ Templeton, J. L. Adv. Organomet. Chem. 1991, 29, 1.

Chart 1. Suggested Limiting Form Contributions to the Structure of the Alkyne Adduct Complexes



Scheme 1



Chart 1)¹⁷ but may also involve contributions from the μ - η^2 : η^1 or μ - η^1 : η^1 bis(carbene) limiting forms (III and IV; Chart 1);^{18a} III resembles structures found in ynamine complexes.^{18b,c} A final possibility is the unbridged fourelectron-donor alkyne V (Chart 1).^{15,19} The ${}^{1}J_{CH}$ value (156.5 Hz) suggests a significant $C(sp) \rightarrow C(sp^2)$ rehybridization in **2e** (${}^{1}J_{CH} = 156$ Hz in CH₂=CH₂ and 249 Hz in HC=CH).^{15,16} Interactions of alkynes with dinuclear complexes containing tripositive group 6 metals have been reported:14,20 they generally give rise to adducts whose structures deviate from the ideal perpendicular bridge geometry, with an unsymmetrical $M_2(\mu$ -C₂R₂) unit and a C–C bond slightly twisted with respect to the M-M axis. The internal carbon chemical shifts of the alkyne bridge carbon atoms in such complexes are <200 ppm, indicating strong deshielding. Examination of the line shapes in variable-temperature ¹H NMR spectra of complexes **2a**,**b** revealed that only the cyclopentadienyl resonances are temperature-dependent. This suggests strongly that the alkyne vector is not perpendicular to the Mo-Mo axis in the typical $\{Mo_2Cp_2(RCCH)(\mu-SMe)_3\}^+$ framework;⁸ consequently, the fluxional motion requires either inversion of the alkyne RC=CH relative to the Mo-Mo axis and/or an exchange of this ligand from one molybdenum site to the other (Scheme 1). In addition, the two cyclopentadienyl signals did not coalesce on warming CD₃CN solutions of **2e**, **f**, suggesting that alkynes with strongly

Scheme 2



electron-withdrawing substituents inhibit the fluxionality. Moderate values for the energy barriers, of 46.8 kJ mol⁻¹ for **2a** (R = Tol) and 50.0 \pm 1 kJ mol⁻¹ for **2b** (R = Ph),²¹ were determined from variable-temperature ¹H NMR studies but are difficult to interpret without a reliable structural model for **2**.

2. Proton Transfer in the Alkyne Adducts [Mo2- $Cp_2(RCCH)(\mu$ -SMe)₃]⁺ (2). Compounds 2a-d were readily deprotonated in the presence of Et₃N to give green solutions of the neutral acetylide derivatives $[Mo_2Cp_2(\mu-\eta^1:\eta^2-C\equiv CR)(\mu-SMe)_3]$ (3). Addition of HBF₄ to dichloromethane solutions of **3** afforded exclusively the expected C_{β} -protonated vinylidene complexes $[Mo_2Cp_2(\mu - \eta^1: \eta^2 - C = CHR)(\mu - SMe)_3](BF_4)$ (4), which were easily deprotonated to regenerate 3 (Scheme 2). The conversion of the Mo₂(III) alkyne adducts **2** into μ -vinylidene species was revealed by ¹H NMR monitoring for complexes $2\mathbf{a} - \mathbf{d}$. A total of 75% of $2\mathbf{a}$ (R = tolyl) slowly transformed into 4a within 3 days at room temperature, but over the same time solutions of 2e and **2f** did not change. It is worth noting that, unlike $tBuC \equiv$ CH, an excess of the terminal alkyne Me₃SiC≡CH reacted with 1 at room temperature within 1 h and afforded the μ -vinylidene complex $[Mo_2Cp_2(\mu-\eta^1:\eta^2=C=$ CH_2 (μ -SMe)₃ (BF₄) (4e). We assume that a 1,2-silvl shift helps to reduce steric crowding and that the product hydrolyzes under moist conditions to yield 4e. Analogous transformations with mononuclear complexes have been reported.²² When it is warmed in acetonitrile, 4e regenerated the bis(acetonitrile) derivative 1, possibly losing acetylene via the reverse vinylidene-alkyne tautomerization. These results indicate that the Mo^{III}₂ alkyne complexes isomerize to the more stable vinylidene adducts at room temperature. However, the reverse reaction, which has been reported for the conversion of the vinylidene species [Mo₂Cp₂- $(CO)_4(\mu - \eta^1: \eta^2 - C = CHR)$ into the related Mo^I₂ alkyne derivative [Mo₂Cp₂(CO)₄(RCCH)],²⁴ may operate at higher temperature. This alkyne-vinylidene isomer-

⁽¹⁶⁾ Bailey, W. I.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. J. Am. Chem. Soc. 1978, 100, 5765.

⁽¹⁷⁾ Hoffman, D. M.; Hoffman, R.; Fisel, C. R. J. Am. Chem. Soc. 1982, 104, 3858.

^{(18) (}a) Spaltenstein, E.; Mayer, J. M. J. Am. Chem. Soc. **1991**, *113*, 7744. (b) Cabrera, E.; Daran, J.-C.; Jeannin, Y. Organometallics **1988**, 7, 2010. (c) Adams, R. D.; Chen, G.; Yin, J. Organometallics **1991**, *10*, 1278.

^{(19) (}a) Chisholm, M. H.; Huffman, J. C.; Heppert, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 5116. (b) Jeffery, J. C.; Moore, I.; Razay, H.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 1581.

^{(20) (}a) Le Grognec, E.; Poli, R.; Richard, P. J. Chem. Soc., Dalton Trans. 2000, 1499. (b) Green, M. L. H.; Mountford, P. Chem. Soc. Rev. 1992, 29. (c) Mountord, P. J. Chem. Soc., Dalton Trans. 1994, 1843. (d) Buhro, W. E.; Chisholm, M. H. Adv. Organomet. Chem. 1987, 27, 311.

⁽²¹⁾ Gutowski, H. S.; Holm, C. H. J. Chem. Phys. 1956, 25, 1228.
(22) (a) Werner, H.; Baum, M.; Schneider, D.; Windmüller, B. Organometallics 1994, 13, 1089. (b) Bullock, R. M. J. Chem. Soc., Chem. Commun. 1989, 165.

^{(23) (}a) Silvestre, J.; Hoffman, R. Helv. Chim. Acta 1985, 68, 1461.
(b) Cadierno, V.; Pilar Gamasa, M.; Gimeno, J.; Pérez-Carreno, E.; Garcia-Granda, S. (c) Connely, N. G.; Geiger, W. E.; Lagunas, M. C.; Metz, B.; Rieger, A. L.; Shaw, M. J. J. Am. Chem. Soc. 1995, 117, 12202. (d) Pérez-Carreno, E.; Paoli, P.; Ienco, A.; Mealli, C. Eur. J. Inorg. Chem. 1999, 1315. (e) Bruce, M. I. Chem. Rev. 1991, 91, 197. (f) El Amouri, H.; Gruselle, M. Chem. Rev. 1996, 96, 1077. (g) Bruce, M. I. Chem. Rev. 1998, 98, 2797.

⁽²⁴⁾ Froom, S. F. T.; Green, M.; Mercer, R. J.; Nagle, K. R.; Orpen, A. G.; Rodrigues, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 3171.



Figure 1. View of a molecule of complex **3a** showing 20% probability ellipsoids for non-hydrogen atoms.

ization at the {Mo₂(μ -SMe)₃} core depends on the electronic properties of the group which is borne by the alkyne as well as on those of the metallic fragment.^{22,23} The 1,2-H shift does not occur when a strongly electron-withdrawing group (e.g., CO₂Me or CF₃) is present in the alkynes, whereas the tautomerization occurs readily when the alkyne contains the electron-releasing *n*-propyl group. In addition, the formation of the initial alkyne adduct **2e** upon addition of HBF₄ to **3e** (R =CO₂Me) shows that the electronic characteristics of the R group may control both the polarity of the acetylide μ - η ¹: η ²-C=CR bridge and the regiospecificity of the electrophilic attack, as has been previously reported for nucleophilic attack.²⁵

The acetylide and vinylidene compounds were identified by NMR spectroscopy, and their structures were confirmed by X-ray analyses of crystals of 3a (R = Tol) and **4b** (R = Ph). The ¹H NMR spectra of the acetylide (3) and vinylidene (4) compounds exhibited the two sets of resonances respectively expected for the $[Mo_2Cp_2(\mu -$ SMe)₃] core and for the R group. The vinylidene bridge μ - η^2 : η^1 -C_{α}=C_{β}HR was characterized by the observation of a ¹H resonance between 6 and 8 ppm, which was assigned to the $=C_{\beta}HR$ group, and of two resonances in the ¹³C NMR spectra, at low field in the carbene (ca. 366 ppm) and in the vinyl (ca. 115 ppm) ranges, which were assigned to C_{α} and C_{β} , respectively. A single resonance was observed for the two cyclopentadienyl groups in the acetylide and vinylidene compounds, suggesting that windshield wiper fluxionality occurs in solution at room temperature.²⁴ The dynamic process could be studied on the NMR time scale only for the vinylidene species: energy barriers of 34.2, 35.9, 42.3, and 61.0 ± 1 kJ mol⁻¹ were determined²¹ for **4a** (R = Tol), 4b (R = Ph), 4d (R = nPr), and 4e (R = H), respectively. Replacement of a hydrogen substituent by an alkyl or aryl group appears to lower the barrier energy for the vinylidene fluxional motion, suggesting that π -electron delocalization through a tolyl or phenyl group facilitates the motion. When R = H, the value is in the range of values determined for neutral dimolyb-



Figure 2. View of the **4b** cation showing 20% probability ellipsoids for non-hydrogen atoms.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in Compounds 3a and 4b

	3a	4b		3a	4b
Mo1-Mo2	2.616(1)	2.622(1)	Mo2-S3	2.472(1)	2.481(1)
Mo1-S1	2.458(1)	2.482(1)	Mo1-C4	2.360(3)	2.268(5)
Mo1-S2	2.449(1)	2.449(1)	Mo1-C5	2.661(3)	2.589(5)
Mo1-S3	2.483(1)	2.462(1)	Mo2-C4	2.068(3)	1.894(5)
Mo2-S1	2.453(1)	2.489(1)	C4-C5	1.238(4)	1.356(6)
Mo2-S2	2.449(1)	2.445(1)	C5-C6	1.443(4)	1.470(7)
Mo1-C4-Mo2	72.1(1)	77.5(2)	C4-C5-C6	168.5(3)	124.9(5)
Mo1-C4-C5	89.8(2)	87.4(3)	C4-C5-Mo1	62.5(2)	61.3(3)
Mo2-C4-C5	160.9(3)	164.6(4)	Mo1-C5-C6	125.2(2)	117.6(3)

denum(I) vinylidene species $[Mo_2Cp_2(CO)_4(\mu-\eta^2:\eta^1-C=CHR)]$,²⁴ suggesting stronger binding of the C=CH₂ moiety to the bimetallic site.

X-ray analyses of 3a and 4b confirm the unsymmetrical *side-on* coordination of the acetylide (Figure 1) and vinylidene (Figure 2) groups which bridge the Mo-Mo bond. The geometries of these complexes will be discussed together (Table 1), since 3a is the deprotonated form of the tolyl analogue of 4b. The lengths of the Mo-Mo single bonds in 3a and 4b are typical of values in $[Mo^{III}_2Cp_2(\mu$ -SR)₃] complexes (the mean length of 42 such bonds is 2.612 Å) and those of the μ -Mo–S bonds are unexceptional.²⁶ The three-electron-donor acetylide ligand in 3a bonds terminally to Mo2 and bonds via the π -electrons of its C=C triple bond to Mo1. The terminal Mo−C≡CR interaction involves enough back-donation from Mo2 to shorten the Mo2-C4 distance to 2.068(3) Å and lengthen the C4-C5 bond (which is also perturbed by its interaction with Mo1) to 1.238(4) Å: for comparison, in $[Mo_2(CCR)_4(PR'_3)_4]$ complexes back-donation into the terminal acetylide ligands is thought to be slight and the average Mo-C and C=C bond lengths are 2.149 and 1.205 Å.²⁷ The π -interaction

^{(26) (}a) Allen, F. H.; Kennard, O. *Chem. Des. Automation News* **1993**, *8*, 31. Version 5.20 of the Cambridge Structural Database with 224 400 structures was used. (b) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *International Tables for Crystallography*; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. C, I.U.Cr.; Table 9.6.

⁽²⁵⁾ Mott, G. N.; Carty, A. J. Inorg. Chem. 1983, 22, 2726.

⁽²⁷⁾ John, K. D.; Miskowski, V. M.; Vance, M. A.; Dallinger, R. F.; Wang, L. C.; Geib, S. J.; Hopkins, M. D. *Inorg. Chem.* **1998**, *37*, 6858.

Scheme 3



metrical (Mo1-C4 = 2.360(3), Mo1-C5 = 2.661(3) Å) and also weak, since the mean length for 2e-donor Mo- $C(\eta^2-C_2R_2)$ bonds is 2.129 Å.^{26b} Protonation of an analogue of 3a at C5 generates the four-electron-donor Mo=C=CHR vinylidene ligand present in 4b. The Mo2-C4 distance (1.894(5) Å) now formally represents a double bond, and it is 0.17 Å shorter than the comparable distance in 3a. Similarly, the C4-C5 bond length (1.356(6) Å) increases, as its order decreases from 3 to 2, and the Mo1–C π -bonds shorten (Mo1–C4 2.268(5), Mo1-C5 2.589(5) Å), presumably as a result of greater back-donation from Mo1. Thus, all three Mo-C distances are shorter in **4b** than **3a**. In **4b**, C5 is sp² hybridized and its attached aromatic ring is in conjugation with the C4-C5 double bond (C4-C5-C6- $C11 = 17.3(8)^{\circ}$). In **3a** and **4b** the coordination of sphybridized C4 carbon atoms is slightly nonlinear but the Mo2-C4-C5 angles (160.9(3)° and 164.6(4)°) are within the range expected for $M_2(\mu - \eta^1: \eta^2 - CCR)$ and $M_2(\mu - \eta^2: \eta^2 - CCR)$ η^{1} : η^{2} -CCHR) groups.^{23e,24} Apart from C4–C5–C6, which changes from 168.5(3) to 124.9(5)°, corresponding bond angles in 3a and 4b are remarkably similar (Table 1). The bridging organic ligands in 3a and 4b resemble those in the zerovalent Mo₂(μ - η^1 : η^2 -CCR) and Mo₂(μ - η^1 : η^2 -CCHR) complexes described by Froom et al., but the Mo⁰–C bond lengths are in general shorter than those in **3a** and **4b** and the Mo⁰-Mo⁰ bond lengths of 3.10-3.12 Å are much longer.²⁴

3. C-S and C-C Couplings Induced by the Addition of RCCH, RNC, and CS₂ to the Alkyne Adduct [Mo₂Cp₂(RCCH)(µ-SMe)₃](BF₄) (2). Reaction of the bis(acetonitrile) compound 1 in dichloromethane with 2 equiv or with a large excess of terminal alkyne RCCH led to brownish green solutions from which sixmembered metallacycle (5) or S-methylthiophenium (6) derivatives were isolated, depending on the nature of the R groups. Interestingly, the same products were formed on reacting the alkyne adducts 2 with an excess (4 equiv) of RCCH (Scheme 3). In contrast, when an excess of RCCH was added to complexes 3a-d or 4ad, no reaction was observed. Complexes 5 and 6 were formulated by a combination of X-ray diffraction and spectroscopic studies. Their molecular structures (see Figures 3 and 4) were reported in a preliminary communication¹⁰ and will not therefore be described here in detail. The structure of the cation in 5a is based on a { $Mo_2Cp_2(\mu$ -SMe)_2} unit which is bridged by an eightelectron-donor CR=CHCR=CHSMe ligand (R = Ph) formed by linking together one SMe bridge and two alkynes, the latter being coupled head-to-tail (Mo1-C4

Figure 3. View of the **5a** cation showing 20% probability ellipsoids for non-hydrogen atoms.¹⁰ As discussed in the text, Mo1 is π -bonded to the C4–C7 butadiene unit.

= 2.24(2) Å, Mo1-C5 = 2.30(2) Å, Mo1-C6 = 2.40(2)Å, Mo1-C7 = 2.45(2) Å; see Figure 3). NMR spectroscopy is in accord with this structure. ¹H NMR spectra exhibited two resonances for the two inequivalent cyclopentadienyl ligands and the set of resonances expected for two R and three SMe groups. The chemical shifts of the SMe groups did not prove unambiguously that one of them had coupled to an alkyne. Two doublets at δ 7.12 and 5.03 (⁴*J*_{HH} = 1.4 Hz) were detected in the ¹H NMR spectrum of **5a** and were assigned to the two protons of the bridging ligand C(R) = CHC(R) = CHSMe. It is worth noting that similar patterns were observed for 5c, suggesting that the same head-to-tail coupling occurs when R is an aliphatic group. The thiophenium derivatives 6 were obtained, but with diminished yields (40-50%) compared to the reactions giving the thiametallacyclic complexes 5a,b (70-75%), when the reactions were conducted at room temperature. This may indicate that the pathway leading to tail-to-tail coupling of the alkyne followed by ring closure was slower than that affording complexes 5a,b. Nevertheless, in the reactions of **2e** and **2f** with excess alkyne $RC \equiv CH$ (R = CO₂Me, CF₃), the only products detectable by ¹H NMR spectroscopy were 6 and an appreciable amount of unreacted alkyne adduct 2e,f (about 30% after 24 h at room temperature). We have previously noted that warming increases the yield of **6a**.¹⁰ The principal structural feature of complex 6a was the presence of the thiophenium ring $\{C_4H_2(CF_3)_2SCH_3\}^+$ in a shallow envelope conformation which is bound to a $\{Mo_2Cp_2(\mu -$



Figure 4. View of a **6a** cation showing 20% probability ellipsoids for non-hydrogen atoms.¹⁰ In the solid there are two crystallographically independent but structurally equivalent cations. One straddles a crystallographic mirror plane; the other (shown here) has no crystallographically imposed symmetry..

Scheme 4



SMe)₂} bimetallic core through the C=C double bonds (Mo···S = 3.386(2)-3.395(2) Å; Mo-C_{α} = 2.161(5)-2.184(6) Å; Mo-C_{β} = 2.249(5)-2.261(6) Å). The ¹H NMR spectrum of **6** displayed one resonance for the two Cp ligands, which is in accord with the symmetrical solid-state structure (Figure 4); a single resonance detected for two protons at about 3.3 ppm indicated the formally tail-to-tail coupling of the two alkynes.

To get additional information on the mechanistic pathway leading to complexes **5** and **6** via C–C and C–S bond formation, we investigated reactions of the alkyne adduct **2b** (R = Ph) with isocyanide substrates. **2b** reacted quantitatively in dichloromethane with 1 equiv of *t*BuNC or xylylNC to give, within 1 h, orange solutions. Orange solids, **7a**,**b**, were obtained upon addition of diethyl ether to the concentrated solution (Scheme 4). Infrared spectra of **7** showed the presence of typical ν (CN) bands at frequencies lower than those of the free ligands;²⁸ these data indicate that an isocyanide molecule is coordinated to a molybdenum atom in **7**. The expected set of resonances of the isocyanide



Figure 5. View of the **7a** cation showing 20% probability ellipsoids for non-hydrogen atoms.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in 7a

(uog) iii vu							
Mo1-Mo2	2.825(1)	N1-C4	1.151(5)				
Mo1-C4	2.104(4)	N1-C5	1.470(6)				
Mo1-C9	2.128(4)	Mo1-S1	2.463(1)				
Mo2-C9	2.293(4)	Mo1-S2	2.441(1)				
Mo2-C10	2.308(4)	Mo2-S1	2.431(1)				
C9-C10	1.399(6)	Mo2-S2	2.434(1)				
S3-C10	1.782(4)	Mo2-S3	2.540(1)				
S3-C3	1.811(5)						
N1-C4-Mo1	172.7(4)	S3-C10-Mo2	75.6(2)				
C4-N1-C5	175.0(5)	Mo1-C9-Mo2	79.3(1)				
C11-C10-Mo2	131.0(3)	C11-C10-S3	122.2(3)				
C10-S3-C3	107.1(2)	C9-C10-Mo2	71.7(2)				
C10-C9-Mo1	130.1(3)	C10-C9-Mo2	72.9(2)				
C3-S3-Mo2	113.2(2)	C9-C10-S3	114.0(3)				
C10-S3-Mo2	61.6(1)						

ligands were detected in the ¹H and ¹³C NMR spectra. In particular, the signals of the CN groups were observed at 166.3 ppm (7a) and 187.1 ppm (7b), in accord with a terminal bonding mode of the isocyanide (Mo-CN-R). The chemical shifts of the unsaturated carbon atoms of the alkyne fall in the sp²-hybridized carbon range (160–100 ppm). The ^{13}C chemical shifts for the σ -bonded (C_a) and the non- σ -bonded (C_b) carbon atoms of the μ -vinyl appear at about 152–150 and 112 ppm, respectively, which are in accord with carbenelike character for C_{α} and sp^3 hybridization at C_{β} .²⁹ X-ray analysis of 7a revealed a C-S bond between the carbon atom bearing the R group of the alkyne ligand and the sulfur atom of one SMe group (S3-C10 = 1.782(4) Å). The structure of 7a (Figure 5 and Table 2) can be regarded as that of a μ - η^{-1} : η^{-3} vinyl-thioether complex in which the vinylic C9–C10 unit is σ -bonded to Mo1 (Mo1-C9 = 2.128(4) Å) and π -bonded to Mo2 (Mo2-C9) = 2.293(4) Å, Mo2-C10 = 2.308(4) Å) and the S3 atom is σ -bonded to Mo2 (Mo2-S3 = 2.540(1) Å). The Mo(1)-Mo(2) length (2.825(1) Å) in 7a is in accord with the electron-counting rules, which require an order of 1 for the Mo(1)-Mo(2) bond, and with the presence of the less sterically constraining MeSCR=CH- bridging group.

⁽²⁸⁾ Pétillon, F. Y.; Schollhammer, P.; Talarmin, J. *J. Organomet. Chem.* **1991**, *411*, 159.

⁽²⁹⁾ Schollhammer, P.; Pétillon, F. Y.; Poder-Guillou, S.; Talarmin, J.; Muir, K. W.; Yufit, D. S. J. Organomet. Chem. **1996**, *513*, 181.



Figure 6. ¹H⁻¹³C 2D HMBC spectrum of 8 (298 K, CDCl₃).

The Mo1-C9 distance is comparable with that observed in the μ - σ : η^2 -vinyl dimolybdenum(II) complex [Mo₂Cp- $(\mu$ -SPh) $(\mu$ - σ : η^2 -C(CH₃)=CH(CH₃))]²⁹ (2.121(8) Å), whereas the Mo2–C9 and Mo2–C10 π bonds in **7a** are slightly shorter than those in the μ - σ : η^2 -vinyl Mo^{II}₂ complex (2.359(8) and 2.397(7) Å), perhaps reflecting the difference in the oxidation states of the molybdenum atoms. The C9-C10 double bond (1.399(6) Å) appears to be lengthened by its coordination to Mo2. Structural features of the terminal tBuNC ligand are unexceptional.³⁰ The μ - η^1 : η^3 structure of the five-membered dimolybdenacycle in **7a** differs from the μ - η^2 : η^2 arrangement found in most related complexes, where the vinylthioether forms part of a thiametallacyclobutene system which is linked to the second metal atom through the vinylic double bond.^{12b-c,31} The μ - η^1 : η^1 coordination of the $-C(CF_3)$ =CHSMe unit in the eight-membered dimolybdenacycle complex $[Mo_2Cp_2\{\mu-\eta^1:\eta^1-C(CF_3)=$ CHSMe₂] shows how the vinyl-thioether ligand can tailor its electron donation to the demands of the metal

atoms.^{11g} To our knowledge, **7a** provides the first crystallographic example of a μ - η^1 : η^3 -CR¹=CR²-SR³ ligand, though μ - η^1 : η^3 -bonding has been proposed to explain the isomerism in [Fe₂(CO)₄{ μ -C(CF₃)=C(CF₃)-SMe}].³²

To find if the regioselectivity of the C-S coupling depends on the nature of the alkyne substituent, as has been previously observed for the coupling of SMe with two alkynes (see above), a solution of the complex 2e in CH₂Cl₂ was treated with 1 equiv of *t*BuNC. A compound 8 in which the isocyanide was coordinated to one molybdenum atom (Scheme 4) was formed. The ¹H-¹³C HMQC and ¹H-¹³C HMBC 2D NMR spectra allowed full assignment of ¹³C chemical shifts and indicated unambiguously that in 8 the sulfur atom of one SMe group was bonded to the carbon of the alkyne bearing the hydrogen atom (Figure 6). The correlation peaks between the methyl protons at 2.37 ppm and the carbon at 100.2 ppm $({}^{3}J_{CH})$ and those between the proton of the CH group at 6.83 ppm, the methanethiolate carbon at 21.7 ppm (${}^{3}J_{CH}$), the carbon bearing the CO₂Me group at 129.6 ppm (${}^{2}J_{CH}$), and the carbon of the CO₂Me group at 175.6 ppm (${}^{3}J_{CH}$), are in accord with a MeSCH=CR-

⁽³⁰⁾ McDermott, L. C.; Muir, K. W.; Pétillon, F. Y.; Poder-Guillou, S.; Schollhammer, P. *Acta Crystallogr*, **1996**, *C52*, 74.

^{(31) (}a) King, J. D.; Mays, M. J.; Pateman, G. E.; Raithby, P. R.; Rennie, M. A.; Solan, G. A.; Choi, N.; Conole, G.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1999**, 4447. (b) Rumin, R.; Guennou, K.; Pétillon, F. Y.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1997**, 1381.

⁽³²⁾ Rumin, R.; Pétillon, F.; Manojlovic-Muir, L.; Muir, K. W. Organometallics 1990, 9, 944.



backbone. Very weak correlations were also detected between the C(CH₃)₃ signal at 1.41 ppm and both the C₅H₅ signal at 5.11 ppm and the carbon signal of the isocyanide at 164.2 ppm (${}^{4}J_{CH}$ and ${}^{3}J_{CH}$). When **8** was left overnight in CDCl₃, quantitative evolution of an organic product was observed. It was identified by its 1 H NMR spectrum and 1 H ${}^{-13}$ C HMBC 2D NMR experiments as the *E* isomer of the vinyl-thioether MeSCH= CHCO₂Me, formally the product of anti-Markownikoff addition of HSMe to the alkyne. The residual organometallic species was not identified (eq 2).



Investigations of the reactivity of the alkyne adducts with carbon disulfide again indicated that the regioselective formation of products with new C–S and C–C bonds was controlled by the R substituent of the alkyne. An excess of CS₂ was added to dichloromethane solutions of complexes **2a,b,e** (Scheme 5). The solutions turned brownish red within 2 h and afforded compounds **9** and **10**, which were identified by NMR spectroscopy, since diffraction-quality crystals could not be obtained. ¹H NMR spectra of **9** and **10** displayed two broad resonances, which were assigned to the cyclopentadienyl ligands. These resonances coalesced upon warming, showing that the complexes were fluxional. Energy



Figure 7. ¹H-¹³C 2D HMBC spectrum of 10 (298 K, CD₃COCD₃).



barrier values of 63.1, 63.8, and $66.3 \pm 1 \text{ kJ.mol}^{-1}$ were determined for **9a**,**b** and **10**, respectively.²¹ The signals of the CH groups were detected at about 6 ppm. Twodimensional heteronuclear ¹H-¹³C inverse-correlation experiments were carried out to characterize 9a and 10. Full assignment of the ¹³C chemical shifts was achieved by means of ¹H-¹³C HMQC and ¹H-¹³C HMBC 2D NMR experiments, which revealed that one carbon atom of the alkyne binds to the sulfur atom of a SMe group and the other to the carbon of CS_2 and, in addition, that the regioselectivity of the C-S coupling depends on the nature of the alkyne substituent. The ¹H-¹³C HMBC 2D NMR spectra of 9a (Figure 7) and 10 are in accord with the respective formation of MeS-C(tol)=CHCS₂⁻ and MeSCH= $C(CO_2Me)CS_2$. No correlation peak between the CH signal and any SMe resonances was detected when R = Tol, whereas in the CO_2Me case, correlations were observed between the SCH₃ signal at 2.66 ppm and the CH resonance at 152.0 ppm (${}^{3}J_{CH}$) and between the CH signal at 7.93 ppm and the carbon of the CS₂ group at 142.5 ppm (${}^{3}J_{CH}$) and the carbon resonance of CO_2 Me at 163.3 ppm (³ J_{CH}) (Figure 7). The vinyl-thioether dithiocarboxylate ligand may bind to the bimetallic site through the three sulfur atoms and the C=C double bond, giving the formally eight-electrondonor ligand (Scheme 5) required by the electroncounting rules.³³ The motion of such a ligand shown in Scheme 6 may explain the temperature dependence of the ¹H NMR spectra of complexes **9** and **10**.

4. Possible Mechanism of Oligomerization of Alkynes at the {Mo₂Cp₂(µ-SMe}₃ Core. Reaction of monosubstituted acetylenes with the bis(nitrile) complex 1 gives first the alkyne complexes 2. This reaction is reversible, since 2 can be converted back to 1 by dissolving it in acetonitrile solution (Scheme 7). The nature of the bonding of the alkyne to the dimolybdenum framework of 2 has not been established in detail. We suggest that the further addition to 2 of an unsaturated molecule L (L = RC=CH, RN=C, S=C=S) produces the intermediate vinyl-thioether complexes **11**. The incoming ligand L bonds to only one of the metal atoms and thereby labilizes a bridging Mo-S bond, into which is inserted the RCCH added in the previous step. Several examples of insertion of an alkyne into an M-SR bond in mononuclear¹¹ and dinuclear complexes¹² have been reported, and it has been shown that vinyl-thioether compounds are intermediates in the formation of thiometallacycles. It is worth noting that under very mild conditions only one isomer of most of the products was obtained in appreciable yield. This strongly suggests that these reactions are highly regioselective and that they depend on a delicate balance involving the electronic and steric properties of both the metallic framework and the alkyne substituents, as is

Scheme 7. Possible Pathways to the Formation of (a) Six-Membered Metallacycle Complexes 5 and thiophenium Complexes 6 and (b) Complexes 7, 8 and 9, 10



often observed in coupling or insertion processes. In the products the most electron-releasing alkyne substituent is adjacent to S: thus, if R = Ph, Tol, *n*Pr the MeSCR= CH ether is formed (11a) via a 1,2-insertion, but when $R = CO_2Me$, CF_3 , i.e., is strongly electronegative, then the MeSCH=CR ether is formed (11b) via a 2,1insertion (Scheme 2). When L = CNR, complexes 7 and **8** are the final products. When $L = CS_2$ is added to **2**, the initially formed **11a** or **11b** gives the expected final product 9 or 10 by insertion of CS₂ into the Mo–C σ bond. When L = RCCH, the second alkyne again inserts into the Mo–C σ -bond of **11a** or **11b** in such a way that the hydrogen-bearing alkyne carbon atom always ends up σ -bonded to molybdenum. For R = CO₂Me, CF₃, the outcome is therefore 12b and reductive elimination gives the thiophenium complexes **6**. When R = Ph, Tol, the same insertion gives 12a and a further 1,4-SMe migration through the metallacycle is needed to get the six-membered metallacycle 5 in which the SMe is borne by the less sterically hindered carbon atom (Scheme 2). This step is strongly reminiscent of the mechanism suggested by Davidson et al. for the formal insertion of an alkyne into the C-S bond of a thio-alkenyl species.^{11d,34}

Conclusion

Transformations of terminal alkynes at the {Mo₂Cp₂- $(\mu$ -SMe)₃⁺} core show that the bis(nitrile) complex $[Mo_2Cp_2(\mu-SMe)_3(CH_3CN)_2](BF_4)$ (1) provides a protected but readily accessible bimetallic site for substrate transformations. Hydrocarbon ligands weaken one Mo-S bond to generate a coordination site together with C-S coupling. Our studies have demonstrated that alkyne dimerization or functionalization can be promoted by a C-S coupling at the bimetallic framework $\{Mo_2Cp_2(\mu -$ SMe)₃. It is noteworthy that fine modifications of such a bimetallic site, involving steric constraint by replacement of two thiolate bridges $(\mu$ -SMe)₂ with a μ - η ²-S₂CH₂ ligand, seem to have a significant influence on its activity.⁷ In conclusion, we have described well-defined syntheses of sulfur-rich dimolybdenum compounds containing alkyne, acetylide, and vinylidene ligands and established their structural relationships using spectroscopic and X-ray diffraction methods. Further transformations of these species are now under investigation.

Experimental Section

General Procedures. The reactions were performed under nitrogen using standard Schlenk techniques. Solvents were deoxygenated and dried by standard methods. IR spectra were recorded on a Perkin-Elmer 1430 spectrophotometer from KBr pellets. Chemical analyses were performed by the Centre de Microanalyses du CNRS, Vernaison, France. NMR spectra (¹H, ¹³C, ¹⁹F) were recorded on either a Bruker AC300 or AMX3 400 spectrometer and were referenced to SiMe₄ (¹H, ¹³C) or CFCl₃ (¹⁹F). The spectroscopic data for **2d** and **5a** have been revised¹⁰ using new ¹H and ¹³C spectra. Literature methods were used for the preparation of [Cp₂Mo₂(μ -SMe)₃(CH₃CN)₂](BF₄) (1).⁹ **Synthesis of [Mo₂Cp₂(\mu-SMe)₃(RCCH)](BF₄) (2).** A solution of complex **1** (0.2 g, 0.32 mmol) in CH₂Cl₂ (15 mL) was stirred in the presence of 1 equiv of RCCH (R = Tol, v = 41 μ L; R = Ph, $v = 35 \mu$ L; R = CH₃C=CH₂, $v = 30.5 \mu$ L; R = nPr, $v = 31.5 \mu$ L; R = CO₂Me, $v = 28.5 \mu$ L) for 30 min at room temperature. The solution turned from red to green (R = CO₂Me) or brownish purple (R = Tol, Ph, CH₃C=CH₂, nPr). The solvent was then concentrated, and Et₂O was added. Brown or green solids precipitated, were collected by filtration, and then were washed with pentane. In a similar procedure, the complex **2f** was obtained by reacting 3 equiv of CF₃CCH with complex **1** as a green powder. Yields: **2a** (R = Tol), 202 mg, 95%; **2b** (R = Ph), 198 mg, 95%; **2c** (R = CH₃C=CH₂), 178 mg, 95%; **2d** (R = nPr), 184 mg, 90%; **2e** (R = CO₂Me), 195 mg, 85%; **2f** (R = CF₃), 165 mg, 80%.

2a. ¹H NMR (CD₃COCD₃, room temperature; δ): 12.90 (s, 1H, TolCC*H*), 7.15, 6.57 (2 × d, 4H, CH₃C₆*H*₄), 6.64 (s, 10H, C₅*H*₅), 2.44 (s, 3H, C*H*₃C₆H₄), 2.31 (s, 3H, SC*H*₃), 2.14 (s, 3H, SC*H*₃), 2.09 (s, 3H, SC*H*₃). ¹H NMR (CD₂Cl₂, 204 K; δ): 12.89 (s, 1H, TolCC*H*), 7.07, 6.35 (2d, *J*_{HH} = 8 Hz, 2 × 2H, CH₃C₆*H*₄), 6.46 (s, 5H, C₅*H*₅), 6.27 (s, 5H, C₅*H*₅), 2.28 (s, 3H, C*H*₃C₆H₄), 2.10 (s, 3H, SC*H*₃), 1.96 (s, 3H, SC*H*₃), 1.90 (s, 3H, SC*H*₃). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C; δ): R*CC*H not observed, 150.0, 137.8, 128.5, 121.6 (CH₃C₆H₄), 101.6 (*C*₅H₅), 43.1, 21.1, 19.2, 18.9 (*C*H₃C₆H₄, 3 × S*C*H₃). Anal. Calcd for C₂₂H₂₇BF₄Mo₂S₃: C, 39.6; H, 4.0. Found: C, 38.4; H, 4.0.

2b. ¹H NMR (CD₂Cl₂, 25 °C; δ): 12.77 (s, 1H, PhCC*H*), 7.32, 7.19, 6.51 (m, 5H, C₆*H*₅), 6.38 (s, 10H, C₅*H*₅), 2.37 (s, 3H, SC*H*₃), 2.06 (s, 3H, SC*H*₃), 1.98 (s, 3H, SC*H*₃). ¹H NMR (CD₂Cl₂, 215 K; δ): 12.88 (s, 1H, PhCC*H*), 7.28–6.44 (m, 5H, C₆*H*₅), 6.47 (s, 5H, C₅*H*₅), 6.27(s, 5H, C₅*H*₅), 2.32 (s, 3H, SC*H*₃), 1.98 (s, 3H, SC*H*₃), 1.92 (s, 3H, SC*H*₃). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C; δ): R*CC*H not observed, 153.1, 128.4, 127.4, 121.3 (*C*₆*H*₅), 101.7 (*C*₃H₅), 43.6 (S*C*H₃), 19.5 (S*C*H₃), 19.1 (S*C*H₃). ¹³C{¹H} NMR (CD₂Cl₂, 208 K; δ): 290.1 and 279.0 (R*CC*H), 152.9, 127.6, 126.5, 120.2 (*C*₆H₅), 101.8, 100.1 (*C*₃H₅), 30.9 (S*C*H₃), 20.0 (S*C*H₃), 19.4 (S*C*H₃). Anal. Calcd for C₂₁H₂₅BF₄-Mo₂S₃: C, 38.6; H, 3.8.Found: C, 37.4; H, 3.8.

Elemental analyses for **2a**,**b** were obtained under nitrogen on three independently prepared pure samples (NMR grade), but unreliable data were obtained, probably because the compounds slowly evolved with partial loss of alkyne, which could explain the slight lowering of the amount percent of carbon.

2c. ¹H NMR (CD₂Cl₂, 25 °C; δ): 12.92 (s, 1H, CH₂=C(CH₃)-CC*H*), 6.40 (s, 10H, C₅*H*₅), 4.64, 4.09 (2s, 2 × 1H, CH₃C=C*H*₂), 2.22 (s, 3H, *CH*₃C=CH₂), 2.10 (s, 3H, SC*H*₃), 2.01 (s, 3H, SC*H*₃), 1.91 (s, 3H, SC*H*₃).

2d. ¹H NMR (CD₃COCD₃, 25 °C; δ): 12.24 (s, 1H, *n*PrCC*H*), 6.54 (s, 10H, C₅*H*₅), 2.23 (s, 3H, SC*H*₃), 2.04 (s, 3H, SC*H*₃), 1.90 (s, 3H, SC*H*₃), 1.14 (m, 2H, (C*H*₂)₂), 0.80 (t, *J*_{HH} = 7.4 Hz, 3H, (CH₂)₂C*H*₃).

2e. ¹H NMR (CD₃COCD₃, 25 °C; δ): 13.17 (s, 1H MeCO₂-CC*H*), 6.82, 6.77 (2 × s, 2 × 5H, 2 × C₅*H*₅), 3.67 (s, 3H, C*H*₃-COOMe), 2.31 (s, 3H, SC*H*₃), 2.17 (s, 3H, SC*H*₃), 2.12 (s, 3H, SC*H*₃). ¹³C NMR (CD₂Cl₂, 25 °C; δ): 272.3 (d, *J*_{CH} = 156.5 Hz, RC*C*H), 266.0 (s, R*C*CH), 185.7 (s, *C*O₂Me), 103.2 (d, *J*_{CH} = 181.0 Hz, *C*₅H₅), 101.7 (d, *J*_{CH} = 181.0 Hz, *C*₅H₅), 43.6 (q, *J*_{CH} = 142.0 Hz, CO₂*C*H₃), 21.3, 21.2 (q, *J*_{CH} = 142.0 Hz, S*C*H₃). IR (KBr pellets; cm⁻¹): 1690 (s) ν (CO), 1150–1050 (s) ν (BF).

2f. ¹H NMR (CD₂Cl₂, 25 °C; δ): 12.96 (s, 1H, CF₃CC*H*), 6.68 (s, 5H, C₅*H*₅), 6.61 (s, 5H, C₅*H*₅), 2.17 (s, 3H, SC*H*₃), 2.15 (s, 3H, SC*H*₃), 2.10 (s, 3H, SC*H*₃). ¹⁹F NMR (CD₂Cl₂, 25 °C; δ): -61.1 (s, CF₃CCH), -149.7 (BF₄⁻). ¹³C{¹H} NMR (CD₃COCD₃, 25 °C; δ): 254.0 (q, $J_{CF} = 30.3$ Hz, CF₃CCH), 263.5 (m, CF₃CCH), 104.2 (C_{5} H₅), 103.5 (C_{3} H₅), 22.9 (S*C*H₃), 22.3 (S*C*H₃). Anal. Calcd for C₁₆H₂₀BF₇Mo₂S₃: C, 29.8; H, 3.1. Found: C, 29.9; H, 3.3.

Synthesis of [Mo_2Cp_2(\mu-SMe)_3(\mu-\eta^1; \eta^2-CCR] (3). To a solution of $[Mo_2Cp_2(\mu-SMe)_3(RCCH)](BF_4)$ (0.2 g: **2a**, 0.30 mmol; **2b**, 0.31 mmol; **2c**, 0.32 mmol; **2d**, 0.32 mmol; **2e**, 0.31

^{(33) (}a) Adams, R. A.; Chen, L.; Wu, W. *Organometallics* **1994**, *13*, 1257. (b) Torres, M. R.; Perales, A.; Ros, J. *Organometallics* **1988**, *7*, 1223.

⁽³⁴⁾ Agh-Atabay, N. M.; Davidson, J. L. J. Chem. Soc., Dalton Trans. 1992, 3531.

mmol) in CH_2Cl_2 was added a slight excess of Et_3N (1.5 equiv). The solution quickly turned green. After the mixture was stirred for a few minutes at ambient temperature, the solvent was evaporated and the compounds **3** were extracted with diethyl ether (3 × 10 mL). The diethyl ether was then removed in vacuo from the pooled extracts. Washing the residue with cold pentane gave **3** as brownish powders. Yields: **3a** (R = Tol), 121 mg, 70%; **3b** (R = Ph), 131 mg, 75%; **3c** (R = CH₃C= CH₂), 118 mg, 70%; **3d** (R = *n*Pr), 110 mg, 65%; **3e** (R = CO_2Me), 68 mg, 40%.

3a. ¹H NMR (CDCl₃, 25 °C; δ): 6.97 (2d, 4H, $J_{HH} = 8.0$ Hz, CH₃C₆H₄), 5.18 (s, 10H, C₅H₅), 2.29 (s, 3H, CH₃C₆H₄), 1.72 (s, 3H, SCH₃), 1.62 (s, 3H, SCH₃), 1.48 (s, 3H, SCH₃).

3b. ¹H NMR (CDCl₃, 25 °C; δ): 7.26 & 7.06 (2m, 5H, C₆H₅), 5.20 (s, 10H, C₅H₅), 1.69 (s, 3H, SCH₃), 1.63 (s, 3H, SCH₃), 1.48 (s, 3H, SCH₃). Anal. Calcd for C₂₁H₂₄Mo₂S₃: C, 44.7; H, 4.0. Found: C, 44.6; H, 4.4.

3c. ¹H NMR (CDCl₃, 25 °C; δ): 5.26 (s, 10H, C₅*H*₅), 5.15, 4.80 (2s, 2 × 1H, CH₃C=*CH*₂), 1.72. (s, 3H, SC*H*₃), 1.60 (s, 6H, 2 × SC*H*₃), 1.42 (s, 3H, *CH*₃C=*C*H₂).

3d. ¹H NMR (Tol- d_8 , 25 °C; δ): 5.07 (s, 10H, C₅ H_5), 1.81 (t, $J_{\text{HH}} = 7.0$ Hz, 2H, $CH_2\text{CH}_2\text{CH}_3$), 1.62 (s, 3H, SC H_3), 1.59 (s, 3H, SC H_3), 1.54 (s, 3H, SC H_3), 1.32 (sext, $J_{\text{HH}} = 7.2$ Hz, 2H, CH₂CH₂CH₃), 0.84 (t, J = 7.4 Hz, 3H, CH₂CH₂CH₃).

3e. ¹H NMR (CDCl₃, 25 °C; δ): 5.52 (s, 10H, C₅H₅), 3.63 (s, 3H, CO₂CH₃), 1.61 (s, 3H, SCH₃), 1.48 (s, 3H, CH₃), 1.37 (s, 3H, CH₃).

Synthesis of [Mo₂Cp₂(μ -SMe)₃(μ - η ¹: η ²-C=CHR](BF₄) (4a– d). To a solution of [Mo₂Cp₂(μ -SMe)₃(μ -CCR)] (0.2 g: **3a**, 0.35 mmol; **3b**, 0.35 mmol; **3c**, 0.38 mmol; **3d**, 0.38 mmol) in Et₂O was added 1 equiv of H[BF₄]·Et₂O. Blue solids of [Mo₂Cp₂(μ -SMe)₃(μ -C=CHR](BF₄) precipitated from the solution and were collected by filtration and then washed with pentane Yields: **4a** (R = Tol), 228 mg, 98%; **4b** (R = Ph), 217 mg, 95%; **4c** (R = CH₃C=CH₂), 222 mg, 95%; **4d** (R = *n*Pr), 225 mg, 96%.

4a. ¹H NMR (CD₂Cl₂, 25 °C; δ): 7.65 (s, 1H, =C=C(Tol)*H*), 7.09 (d, 2H, CH₃C₆*H*₄), 6.90 (d, 2H, CH₃C₆*H*₄), 6.02 (s, 10H, C₅*H*₅), 2.29 (s, 3H, C*H*₃C₆H₄), 1.85 (s, 3H, SC*H*₃), 1.68 (s, 3H, SC*H*₃), 1.50 (s, 3H, SC*H*₃). Anal. Calcd for C₂₂H₂₇BF₄Mo₂S₃: C, 39.6; H, 4.0. Found: C, 37.4; H, 4.7.

4b. ¹H NMR (CD₃COCD₃, 25 °C; δ): 7.99 (1H, s, =C=C(Ph)-H), 4.78–7.15 (5H, m, C₆H₅), 6.28 (10H, s, C₅H₅), 1.93 (3H, s, SCH₃), 1.76 (3H, s, SCH₃), 1.55 (3H, s, SCH₃). ¹³C{¹H} NMR (CDCl₃, 25 °C; δ): 368.4 (=*C*=CHPh), {(131.6, s), (130.3, dt, $J_{CH} = 162.0$ Hz, $J_{CH} = 7.3$ Hz), (129.1, dm, $J_{CH} = 164.0$ Hz), (128.9, dm, $J_{CH} = 165.0$ Hz) C_6 H₅}, 115.4 (d, $J_{CH} = 163.0$ Hz, =C=CHPh), 98.2 (d, $J_{CH} = 181.0$ Hz, C_5 H₅), 19.4 (q, $J_{CH} = 141.0$ Hz, SCH₃), 10.6 (q, $J_{CH} = 141.0$ Hz, SCH₃), 6.7 (q, $J_{CH} = 141.0$ Hz, SCH₃). Anal. Calcd for C₂₁H₂₅BF₄Mo₂S₃: C, 38.6; H, 3.8. Found: C, 37.8; H, 4.0.

Repeated poor analytical results were obtained for spectrospically (NMR) pure samples of 4a, b for reasons similar to those for 2a, b (see above).

4c. ¹H NMR (CD₃COCD₃, 25 °C; δ): 7.46 (s, 1H, =C=CR*H*), 6.27 (s, 10H, C₅*H*₅), 5.31, 4.97 (2 × m, 2 × 1H, CH₃C=C*H*₂), 1.92. (s, 3H, SC*H*₃), 1.68 (s, 3H, SC*H*₃), 1.58 (s, 3H, SC*H*₃), 1.52 (q, *J*_{HH} = 0.7 Hz, 3H, *CH*₃C=CH₂).

4d. ¹H NMR (CD₂Cl₂, 25 °C; δ): 6.60 (s, broad, 1H, =C= C(nPr)*H*), 6.07 (s, 10H, C₅*H*₅), 1.89 (s, 3H, SC*H*₃), 1.68 (m, 2H, (C*H*₂)₂), 1.57 (s, 3H, SC*H*₃), 1.48 (m, 2H, (C*H*₂)₂), 1.45 (s, 3H, SC*H*₃), 0.93 (t, *J*_{HH} = 7.2 Hz, 3H, (CH₂)₂C*H*₃). ¹³C NMR (CD₂Cl₂, 25 °C; δ): 365.3 (=*C*=CH(*n*Pr)), 114.2 (d, *J*_{CH} = 163.2 Hz, =C=*C*H(*n*Pr)), 97.4 (d, *J*_{CH} = 168.0 Hz, *C*₅H₅), 25.0 (t, *J*_{CH} = 128.5 Hz, *C*H₂), 13.4 (q, *J*_{CH} = 125.5 Hz, *C*H₃), 9.9 (q, *J*_{CH} = 142.0 Hz, S*C*H₃), 6.3 (q, *J*_{CH} = 141.1 Hz, S*C*H₃). One SCH₃ has not been assigned.

Synthesis of $[Mo_2Cp_2(\mu-SMe)_3(\mu-\eta^1: \eta^2-C=CH_2](BF_4)$ (4e). A solution of complex 1 (0.2 g, 0.32 mmol) in CH₂Cl₂ (15 mL) was stirred with an excess of Me₃SiCCH ($v = 250 \ \mu$ L) for 1 h at 25 °C. The solution turned from red to blue-green. The solvent was then concentrated, and Et₂O was added. A blue solid precipitated. It was collected by filtration and then washed with pentane. Yield: 4e (R = H), 175 mg, 95%,

4e. ¹H NMR (CD₂Cl₂, 25 °C; δ): 6.44 (s, broad, 5H, C₅*H*₅), 6.00 (s, broad, 5H, C₅*H*₅), 5.64 and 5.20 (AB, *J*_{HH} = 18.7 Hz, 2H, =C=*CH*₂), 1.95 (s, 3H, SC*H*₃), 1.60 (s, 3H, SC*H*₃), 1.42 (s, 3H, SC*H*₃). ¹³C{¹H} NMR (CDCl₃, 25 °C; δ): 371.5 (=*C*=CH₂), 99.9 (*C*₅H₅), 94.3 (*C*₅H₅), 87.1 (=*C*=*C*H₂), 21.8 (S*C*H₃), 9.4 (S*C*H₃), 6.8 (S*C*H₃).

Reaction of [Mo₂Cp₂(\mu-SMe)₃(RCCH)](BF₄) (2a,b,d–f) with Additional RCCH. A solution of the alkyne complex [Mo₂Cp₂(μ -SMe)₃(RCCH)](BF₄) (0.2 g: **2a**, 0.30 mmol; **2b**, 0.31 mmol; **2d**, 0.32 mmol; **2e**, 0.31 mmol; **2f**, 0.31 mmol) in CH₂Cl₂ (15 mL) was stirred in the presence of an excess (4 equiv) of the same RCCH alkyne (R = Tol, $v = 154 \ \mu$ L; R = Ph, $v = 136 \ \mu$ L; R = nPr, $v = 126 \ \mu$ L; R = CO₂Me, $v = 110 \ \mu$ L; CF₃¹⁰) for 24 h at room temperature. The solution turned brownish green. The solvent was then concentrated, and Et₂O was added. Brownish green solids precipitated. They were collected by filtration and then washed with pentane. Yields: **5a** (R = Tol), 164 mg, 70%; **5b** (R = Ph), 175 mg, 75%; **5c** (R = *n*Pr), 143 mg, 65%; **6a** (R = CF₃), 96 mg, 42% yield; **6b** (R = CO₂Me), 100 mg, 45%.

5a.¹⁰ ¹H NMR (CD₃COCD₃, 25 °C; δ): [7.80 (d, $J_{\text{HH}} = 8.5$ Hz, 2H), 7.36 (d, $J_{\text{HH}} = 8.5$ Hz, 2H), 7.02 (d, $J_{\text{HH}} = 8.5$ Hz, 2H), 6.58 ($J_{\text{HH}} = 8.5$ Hz, 2H), 7.02 (d, $J_{\text{HH}} = 8.5$ Hz, 2H), 6.58 ($J_{\text{HH}} = 8.5$ Hz, 2H, d)] 2 × C₆H₄CH₃, 7.12 and 5.03 (2 × d, $J_{\text{HH}} = 1.4$ Hz, 2 × 1H, -CH=CRCH=CR-), 5.56 (s, 5H, C₅H₅), 5.39 (s, 5H, C₅H₅), 2.45, 2.42, 2.28, 2.24, 1.86 (5 s, 5 × 3H, 2 × C₆H₄CH₃ and 3 × SCH₃). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C; δ): 141.7, 136.6, 136.5, 136.0, 132.2, 130.1, 129.4, 128.4, 127.2, 126.7 (*TolC=CH=CTol=CHSMe*), 98.5 (C_5 H₅), 94.3 (C_5 H₅), 21.2, 20.9, 26.1, 22.9, 19.7 (2 × C₆H₄CH₃ + 3 × SCH₃). Anal. Calcd for C₃₁H₃₅BF₄Mo₂S₃: C, 47.6; H, 4.5. Found: C, 47.3; H, 4.4.

5b. ¹H NMR (CD₃COCD₃, 25 °C; δ): δ 7.91 and 7.53 (m, 5H, *Ph*C=CH=*CPh*=CHSMe), 7.19 & 6.70 (m, 5H, *Ph*C=CH= *CPh*=CHSMe), 7.14 (d, *J*_{HH} = 1.3 Hz, 1H, PhC=*CH*=C(Ph)= *CH*SMe), 5.60 (s, 5H, C₅*H*₅), 5.40 (s, 5H, C₅*H*₅), 5.05 (d, *J*_{HH} = 1.3 Hz, 1H, PhC=*CH*=C(Ph)=*CH*SMe), 2.45 (s, 3H, SC*H*₃), 2.27 (s, 3H, SC*H*₃), 1.87 (s, 3H, SC*H*₃). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C; δ): 152.8, 138.9, 132.4, 130.9, 130.0, 129.2, 127.9, 127.1, 126.9, 126.8 (*PhC*=*C*H=*CPh*=*C*HSMe), 98.6 (*C*₅H₅), 94.4 (*C*₅H₅), 23.8 (S*C*H₃), 15.7 (S*C*H₃), 11.1 (S*C*H₃). Anal. Calcd for C₂₉H₃₁BF₄Mo₂S₃: C, 46.2; H, 4.1. Found: C, 46.4; H, 4.2.

5c. ¹H NMR (CDCl₃, 25 °C; δ): 6.35 (s, broad, 1H, (*n*Pr)C= C*H*=C(*n*Pr)=C*H*SMe), 5.50 (s, 5H, C₅*H*₅), 5.13 (s, 5H, C₅*H*₅), 4.29 (s, broad, 1H, (*n*Pr)C=C*H*=C(*n*Pr)=C*H*SMe), 2.40 (m, 2H, (C*H*₂)₂), 2.26 (s, 3H, SC*H*₃), 1.90 (m, 4H, (C*H*₂)₂), 1.88 (s, 3H, SC*H*₃), 1.79 (s, 3H, SC*H*₃), 1.40 (m, 2H, (C*H*₂)₂), 1.17 (t, *J*_{HH} = 7.2 Hz, 3H, C*H*₃), 0.96 (t, *J*_{HH} = 7.2 Hz, 3H, C*H*₃).

6a.¹⁰ ¹H NMR (CD₃COCD₃, 25 °C; δ): 5.97 (s, 10H, C₅*H*₅), 3.38 (s, 2H, C₄(CF₃)₂*H*₂SCH₃⁺), 2.73 (s, 3H, C₄(CF₃)₂H₂S*CH*₃⁺), 2.33 (s, 3H, SC*H*₃), 2.10 (s, 3H, SC*H*₃). ¹⁹F NMR (CD₃COCD₃, 25 °C; δ): -51.3 (s, C₄(C*F*₃)₂H₂SCH₃⁺), -150.3 (s, B*F*₄⁻). Anal. Calcd for C₁₉H₂₁BF₁₀Mo₂S₃: C, 30.9; H, 2.8. Found: C, 30.6; H, 3.0.

6b. ¹H NMR (CD₃COCD₃, 25 °C, δ): 5.84 (s, 10H, C₅*H*₅), 3.67 (s, 2H, C₄(CO₂C*H*₃)₂H₂SCH₃⁺), 3.33 (s, 2H, C₄(CO₂-CH₃)₂*H*₂SCH₃⁺), 2.70 (s, 3H, C₄(CO₂CH₃)₂H₂S*CH*₃⁺), 2.13 (s, 3H, SC*H*₃), 1.95 (s, 3H, SC*H*₃).

Reaction of [Mo₂Cp₂(\mu-SMe)₃(RCCH)](BF₄) (2b,e) with **RNC (R = tBu, Xylyl).** A solution of [Mo₂Cp₂(μ -SMe)₃-(PhCCH)](BF₄) (2b; 0.2 g, 0.30 mmol) in CH₂Cl₂ (15 mL) was stirred with 1 equiv of RNC (R = tBu, $v = 34 \mu$ L; R = xylyl, m= 39.3 mg) for 1 h at room temperature. The solution readily turned orange. The solvent was then concentrated, and Et₂O was added. Orange solids precipitated. They were collected by filtration and then washed with pentane. Yields: **7a** (R = Ph, L = tBuNC), 198 mg, 90%; **7b** (R = Ph, L = xylylNC), 200 mg, 85%. The same procedure was applied to **2e** (0.2 g, 0.31 mmol)

	3a	4b	7a
empirical formula	$C_{22}H_{26}Mo_2S_3 \cdot 0.5C_5H_{12}$	$C_{21}H_{25}BF_4Mo_2S_3$	$C_{27}H_{36}BCl_2F_4Mo_2NS_3$
fw	614.56	652.28	820.34
cryst syst	monoclinic	monoclinic	monoclinic
space group	Cc	$P2_1/c$	$P2_1/c$
a, Å	14.1852(8)	15.7730(15)	10.2490(6)
b, Å	22.5726(10)	8.5305(6)	12.2493(12)
<i>c</i> , Å	7.9974(3)	17.7108(7)	25.9798(17)
β , deg	90.695(4)	90.285(6)	91.212(5)
<i>V</i> , Å ³	2560.6(2)	2383.0(3)	3260.9(4)
Ζ	4	4	4
$D_{ m calcd}$, Mg/m ³	1.594	1.818	1.671
μ , mm ⁻¹	1.234	1.354	1.167
F(000)	1244	1296	1648
cryst size, mm	0.47 imes 0.16 imes 0.11	$0.30\times0.28\times0.13$	0.30 imes 0.13 imes 0.05
heta range, deg	2.9 - 30.4	2.3 - 27.0	2.3 - 26.9
index ranges	$-20 \le h \le 20$	$-20 \le h \le 2$	$-13 \le h \le 13$
	$-19 \leq k \leq 32$	$-10 \leq k \leq 1$	$-2 \le k \le 15$
	$-11 \leq l \leq 6$	$-22 \leq l \leq 22$	$-3 \le l \le 33$
no. of rflns collected	8598	6768	8766
no. of indep rflns	5221 ($R_{\rm int} = 0.015$)	5206 ($R_{\rm int} = 0.035$)	7037 ($R_{\rm int} = 0.020$)
no. of obsd rflns with $I > 2\sigma(I)$	4835	3502	5077
abs cor	analytical	<i>t</i> -scans	analytical
$T_{\rm max}, T_{\rm min}$	0.896 - 0.669	0.769 - 0.709	0.950 - 0.906
no. of data/params	5221/255	5206/284	7037/365
goodness of fit on F ²	1.033	0.918	1.010
R1, wR2 $(I \geq 2\sigma(I))$	0.022, 0.056	0.042, 0.073	0.039, 0.093
R1, wR2 (all data)	0.028, 0.058	0.101, 0.083	0.071, 0.106
Flack param	0.07(3)		
Δho range, e A^{-3}	+0.43 to -0.30	+0.66 to -0.50	+0.85 to -0.88

^{*a*} All measurements were made at 20 °C with Mo K α radiation, $\lambda = 0.710$ 73 Å, on a Nonius CAD4 diffractometer.

and afforded in the presence of an equimolar amount of *t*BuNC ($v = 35 \ \mu$ L) the complex **8** as an orange powder Yield: 204 mg, 92%.

7a. ¹H NMR (CD₂Cl₂, 25 °C; δ): 7.37 & 7.0 (m, 5H, C₆H₅), 6.76 (s, 1H, MeSCR=CH), 5.21 (s, 5H, C₅H₅), 5.11 (s, 5H, C₅H₅), 2.16 (s, 3H, SCH₃), 1.96 (s, 3H, SCH₃), 1.59 (s, 3H, SCH₃), 1.36 (s, 9H, C(CH₃)₃). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C; δ): 166.3 (*C*NC-(CH₃)₃), 151.8 (MeSCR=CH), 139.0, 129.2, 128.9, 127.9 (C₆H₅), 111.7 (MeSCR=CH), 93.8 (C₅H₅), 91.4 (C₅H₅), 59.1 (C(CH₃)₃), 29.9 (C(CH₃)₃), 23.9 (SCH₃), 22.4 (SCH₃), 14.1 (SCH₃). IR (KBr pellets; cm⁻¹): 2120 (s) ν (CN), 1150–1050 (s) ν (BF). Anal. Calcd for C₂₆H₃₄NBF₄Mo₂S₃·CH₂Cl₂: C, 39.5; H, 4.4; N, 1.7. Found: C, 39.4; H, 4.4, N, 2.2.

7b. ¹H NMR (CD₂Cl₂, 25 °C; δ): 7.4–6.9 (m, 8H, C₆*H*₃(CH₃)₂ and C₆*H*₅), 6.86 (s, 1H, MeSCR=*CH*), 5.27 (s, 5H, C₅*H*₅), 5.26 (s, 5H, C₅*H*₅), 2.37 (s, 6H, C₆H₃(C*H*₃)₂), 2.28 (s, 3H, SC*H*₃), 1.88 (s, 3H, SC*H*₃), 1.67 (s, 3H, SC*H*₃). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C; δ): 187.1 (*C*NC₆H₃(CH₃)₂), 150.8 (MeS*C*R=*C*H), 139.0–127.0 (*C*₆H₃(CH₃)₂ and *C*₆H₅), 111.7 (MeSCR=*C*H), 94.2 (*C*₅H₅), 92.1 (*C*₅H₅), 24.9 (S*C*H₃), 23.1 (S*C*H₃), 19.5 (CNC₆H₃(*C*H₃)₂), 14.5 (S*C*H₃). IR (KBr pellets; cm⁻¹): 2060 (s) ν (CN), 1150–1050(s) ν (BF). Anal. Calcd for C₃₀H₃₄NBF₄Mo₂S₃·CH₂Cl₂: C, 42.8; H, 4.1; N, 1.6. Found: C, 42.6; H, 4.1, N, 1.7.

8. ¹H NMR (CDCl₃, 25 °C; δ): 6.83 (s, 1H, CR=CHSCH₃), 5.45 (s, 5H, C₅H₅), 5.11 (s, 5H, C₅H₅), 3.58 (s, 3H, CO₂CH₃), 2.37 (s, 3H, CR=CHSCH₃), 2.26 (s, 3H, SCH₃), 1.71 (s, 3H, SCH₃), 1.41 (s, 9H, C(CH₃)₃). ¹³C NMR (CDCl₃, 25 °C; δ): 175.6 (CO₂CH₃), 164.2 (CNC(CH₃)₃), 129.6 (CR=CHSCH₃), 100.2 (CR=CHSCH₃), 93.7 (C₅H₅), 91.5 (C₅H₅), 58.5 (C(CH₃)₃), 51.8 (CO₂CH₃), 29.6 (C(CH₃)₃), 23.6 (SCH₃), 21.7 (CR=CHSCH₃), 13.4 (SCH₃).

Reaction of [Mo₂Cp₂(\mu-SMe)₃(RCCH)](BF₄) (2a,b,e) with CS₂. A solution of the complex [Mo₂Cp₂(μ -SMe)₃(RCCH)](BF₄) (0.2 g: 2a, 0.30 mmol; 2b, 0.31 mmol; 2e, 0.31 mmol) in CH₂Cl₂ (15 mL) was stirred with excess CS₂ (2 mL) for 2 h at room temperature. The solution turned brownish red. The solvent was then concentrated, and Et₂O was added. Brown solids precipitated. They were collected by filtration and then washed with pentane. Yields: **9a** (R = Tol), 184 mg, 80%; **9b** (R = Ph), 186 mg, 85%; **10** (R = CO₂Me), 189 mg, 86%.

9a. ¹H NMR (CD₃COCD₃, 25 °C; δ): 7.31–7.26 (m, 4H, C₆*H*₄), 6.44 (s, broad, 5H, C₅*H*₅), 6.08 (s, 1H, -CH=CRSCH₃), 5.76 (s, broad, 5H, C₅*H*₅), 2.36 (s, 3H, C₆H₄C*H*₃), 2.19 (s, 3H, SC*H*₃), 2.14 (s, 3H, SC*H*₃), 2.06 (s, 3H, -CH=CRSC*H*₃). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C; δ): 146.6 (-CH=*C*R-SCH₃), 142.6 (*C*S₂), 140.0, 135.2, 130.1, 129.3 (*C*₆H₄), 133.3 (-CH=CRSCH₃), 103.1 (*C*₅H₅), 94.6 (*C*₅H₅), 26.2 (S*C*H₃), 21.1 (C₆H₄CH₃), 16.8 (-CH=CRS*C*H₃), 10.3 (S*C*H₃). Anal. Calcd for C₂₃H₂₇BF₄Mo₂S₅·CH₂Cl₂: C, 34.7; H, 3.7. Found: C, 34.8; H, 3.5.

9b. ¹H NMR (CD₃COCD₃, 25 °C; δ): 7.42 (m, 5H, C₆H₅), 6.28 (s, broad, 5H, C₅H₅), 6.09 (s, 1H, -CH=CR-), 5.76 (s, broad, 5H, C₅H₅), 2.14 (s, 3H, SCH₃), 2.10 (s, 3H, SCH₃), 2.05 (s, 3H, SCH₃), ¹³C{¹H} NMR (CD₂Cl₂, 25 °C; δ): 147.6, 142.3, 137.3, 132.3, 129.7, 129.2, 129.0 ($C_6H_5 + -CH=CR - + CS_2$), 102.2 (C_5H_5), 93.9 (C_5H_5), 26.5 (SCH₃), 19.7 (SCH₃), 10.9 (SCH₃). IR (KBr pellets; cm⁻¹): 1150–1050 (s) ν (BF). Anal. Calcd for C₂₂H₂₅BF₄Mo₂S₅·CH₂Cl₂: C, 33.9; H, 3.3. Found: C, 34.2; H, 3.5.

10. ¹H NMR (CD₃COCD₃, 25 °C; δ): 7.93 (s, 1H, CH₃SC*H*= CR-), 6.34 (s, broad, 5H, C₅*H*₅), 5.74 (s, broad, 5H, C₅*H*₅), 3.72 (s, 3H, CO₂C*H*₃), 2.66 (s, 3H, C*H*₃SCH=CR), 2.17 (s, 3H, SC*H*₃), 2.15 (s, 3H, SC*H*₃). ¹³C{¹H} NMR (CD₃COCD₃, 25 °C; δ): 152.0 (CH₃S*C*H=CR-), 163.3 (*C*O₂CH₃), 142.5 (*C*S₂), 127.1 (CH₃SCH=*C*R-), 102.9 (*C*₅H₅), 94.4 (*C*₅H₅), 52.6 (CO₂*C*H₃), 25.7 (*C*H₃SCH=CR), 20.5 (S*C*H₃), 10.2 (S*C*H₃). Anal. Calcd for C₁₈H₂₃BF₄Mo₂O₂S₅: C, 30.4; H, 3.2. Found: C, 30.2; H, 3.3.

Crystal Structure Determinations of 3a, 4b, and 7a. Pertinent data are summarized in Table 3. In general, the structures were refined with anisotropic displacement parameters for non-hydrogen atoms and hydrogen atoms were subject to riding constraints during refinement.³⁵ However, the hydrogen atoms attached to C5 in **4b** and to C9 in **7a** were located in difference syntheses and their parameters were then

⁽³⁵⁾ Programs used: Sheldrick, G. M. SHELX97–Programs for Crystal Structure Analysis (Release 97-2); Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998. Farrugia, L. J. WinGX–A Windows Program for Crystal Structure Analysis. J. Appl. Crystallogr. **1999**, *32*, **8**37.

successfully refined. The crystal of **3a** contained highly disordered solvent, believed to be *n*-pentane, which was modeled approximately by including the seven most highly populated atomic sites in the structure factor calculations as C atoms with 50% occupancy. The position of each site was taken from a difference synthesis, and subsequently, only its $U_{\rm iso}$ parameter was refined. Crystals of **7a** contain ordered dichloromethane.

Acknowledgment. We are grateful to N. Kervarec and R. Pichon for the recording of two-dimensional NMR spectra on a Bruker DRX 500 (500 MHz) spectrometer.

We thank the CNRS, the EPSRC, Glasgow University, and the University of Brest for financial support.

Supporting Information Available: For **3a**, **4b**, and **7a**, tables giving details of structure determinations, non-hydrogen atomic positional parameters, all bond distances and angles, anisotropic displacement parameters, and hydrogen atomic coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000966J